and a 10° C./min ramp to 260°, then held for 5 min. A constant flow of 30 cm/sec was used with a starting pressure of 16.87 psig. The column used was an Agilent WaxEtr 60 m×320 μm with a 1.0 μm film thickness. The detector was set at 275° C. with 40 ml/min H_2 and 450 ml/min air. The carrier mode was constant with column and makeup flow combined for 45 ml/min; makeup gas was nitrogen.

Calibration was done with a 3-point calibration using the following components: phenol, cis-1,2 cyclohexanol, acetic acid, 2-methoxycyclohexanol, cyclohexanol, furfural, guaiacol, cyclohexanone, 2-butanol, ethanol, tetrahydrofuran, 2-methyl-tetrahydrofuran, cyclohexyl-methyl-ether. The standards were diluted in a 80/20 acetone/water solution. Uncalibrated components were given a semi-quantitative value based on similar components having the same number of carbon atoms.

Gas chromatography—mass spectrometry was used for qualitative analysis using an Agilent model 5890 GC running the same temperature program described above and the identical column, coupled with an Agilent model 5972 Mass Selective Detector (MSD). The MSD was scanning at a rate of 1.6 scans/sec from 20-500 atomic mass units. The mass data was analyzed using Agilent Chemstation software G1701AA version A02.00. The compound peaks were determined using a Probability-Based Matching (PBM) algorithm. Two libraries were used to identify peaks, the Wiley275 library (275,000 compounds) and an in house developed library of compounds we had determined from previous bio-oil analysis efforts[10]. A PBM library search proceeds by searching mass spectral libraries using the probability-based matching algorithm developed at Cornell University. The search algorithm compares an unknown spectrum to each reference spectrum using the reverse search technique. A reverse search technique verifies that the main peaks in a reference spectrum are present in the unknown spectrum.

Pyrolysis Oil Hydrotreating: Process Performance

The apparatus used for hydrotreating bio-oil in a continuous (not a batch) process was a fixed catalytic bed in a tubular reactor operated with concurrent down-flow of bio-oil and hydrogen gas. A bench-scale unit with a 400-milliliter fixed catalyst bed was assembled in our lab for process tests with different feedstocks, catalysts, and processing conditions. The bio-oil was fed to the reactor by a high-pressure metering piston pump. The pump's feed cylinder, feed lines, and the reactor were all maintained at temperature by a circulating hot oil system. Pressure in the reactor was maintained by a dome-loaded back-pressure regulator. Products exiting the reactor were cooled, and the condensed liquids collected in sampling cylinders, which were periodically drained. The gas product was vented through a meter, and intermittent samples were drawn for analysis.

During the tests using the palladium catalysts, the bio-oils were easily processed in the reactor system. The carbon-supported catalyst had 2 wt % palladium and an apparent bulk density of 0.5 g/mL. Processing temperature set points in the range of 200 to 360° C. were tested. A significant exothermic reaction caused the catalyst beds to operate at up to 20° C. higher than the set point.

Process Results

Tests were performed using a white softwood bio-oil obtained from Dynamotive, which during storage had separated into two phases. These tests proceeded smoothly with all reactor components functioning as designed. The process data are summarized in Table Y. The temperatures were measured temperatures, not the set point temperatures.

TABLE Y

Hydrotreating of Softwood Bio-oil, Heavy Fraction, with Edge-Coated 1.5% Pd/C Catalyst

Run Conditions and Results					
Temperature, ° C.	312	313	347	347	379
Pressure, psig	1910	1917	1911	1913	1939
Liquid Hourly Space Velocity, L/L/hr	0.22	0.22	0.22	0.22	0.22
Carbon Balance, %	94	83	94	92	90
Material Balance, %	96	93	97	97	94
Product Yield, g/g of dry feed	0.80	0.75	0.75	0.74	0.72
Product Yield (mass balance normalized) g/g of dry feed	0.83	0.81	0.77	0.76	0.77
H_2 Consumption, L/L bio-oil feed	156	232	296	237	319
Deoxygenation, %	48.2	52.0	61.3	58.7	65.3
Water in oil, wt %	4.93	5.44	2.91	2.91	2.16
Aqueous phase carbon, wt %	13.56	13.13	10.70	10.40	10.99
Oxygen in dry oil, wt %	16.99	17.61	12.52	14.28	12.52
Density of product oil, g/mL	1.122	1.087	1.03	~1.03	0.946
Total Acid Number, mg KOH/g oil			42.0		36.5

Note:
Product Yield includes:
(1) Oil fraction of oil product (water free)
(2) Organics in aqueous phase.

What is claimed:

1. A product mixture made from a method comprising:

providing a bio-oil;

providing hydrogen (H2); and

reacting the bio-oil and hydrogen over a catalyst at a temperature of more than 200° C.;

wherein the catalyst comprises Pd; and

producing a liquid oil from the reaction of the bio-oil and hydrogen.

2. A method of hydrogenation of furfural, guaiacol, or a substituted guaiacol, comprising:

providing a liquid comprising furfural, guaiacol or a substituted guaiacol;

providing hydrogen (H2); and

reacting the furfural, guaiacol, or a substituted guaiacol with hydrogen over a catalyst at a temperature of more than 200° C.;